Identification of the active catalyst phases of the bimetallic Cobalt and Palladium Zinc oxides for the reforming reactions of alcohols.

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Introduction

Pd/ZnO and Co/ZnO have been shown to be effective alcohol reforming catalysts[1-3]and thus can be used to make hydrogen from renewable feedstocks. Recent studies have shown that an active component of the Pd/ZnO system under CH_3OH reforming conditions is a PdZn alloy[4] which is formed under reaction conditions[5]. The precise roles of PdZn alloy and the ZnO [6]support in the decomposition, Eqn 1, and reverse water-gas-shift (RWGS), Eqn 2,reactions is unknown.

$$CH_3OH \rightleftharpoons CO + 2H_2 \quad (1) \qquad CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (2)$$

Also unknown is the role of these zinc alloys (especially CoZn) in the reforming of CH_3CH_2OH, which includes a more complex decomposition step which also requires C-C bond breaking, Eqn 3, $CH_3CH_2OH + H_2O \rightleftharpoons 2CO + 4H_2$ (3)

In an effort to better understand the role of Pd and Co zinc-alloys in the reforming reactions of both CH_3OH and CH_3CH_2OH we have prepared single phase, unsupported, bimetallic zinc alloys of different compositions so as to investigate the effect of alloy composition on catalytic activity. Partial oxidation of the metal alloy also allows us to generate a ZnO phase in-situ, allowing us to identify the most active and stable phases for alcohol reforming catalysts. The activity of the aerosol-derived bimetallic catalysts will also be examined for the posited elementary steps in the reforming reaction. In addition, In-situ techniques such as EXAFS will be used to attempt to identify the chemical and structural nature of the active sites on the bimetallic particles, before, during, and after reaction.

Materials and Methods

Different compositions of PdZn(Pd:Zn~0.9-1.1) CoZn(Co:Zn~1.1-1.5) as well as pure-metal particles were synthesized from high-purity commercial nitrates using an aerosol process. The particles were characterized using XRD, XPS, SEM, STEM/EDS. Surface area and site density was estimated using chemisorption and CO oxidation studies under both static and flowing gas conditions. Reaction studies were carried out in a packed-bed microreactor analyzed by inline GC and MS as well as a thermal environmental DRIFTS cell.

Results and Discussion

The aerosol synthesis method with air as a carrier gas produces metallic spherical particles. Since the liquid precursors are well mixed, the particle composition is uniform across the entire batch. Reduction in flowing N_2/H_2 yields unagglomerated dimpled spheres of 100-300nm diameter, Fig. 1a, XRD analysis shows that a single phase metal alloy has been generated (Fig. 1b) and SEM-EDS analysis reveals a uniform homogenous composition across the sample. Preliminary Methanol reforming tests in a micro reactor show that catalysts with stoichiometric Pd:Zn deactivate quickly, losing about 80% activity over several hours, while maintaining good CO_2 selectivity. In contrast, 1:1.2: PdZn does not deactivate over the same time on stream and maintains even better selectivity to CO_2. Examination of the used catalyst having excess Zn, Fig 1b, reveals the formation of a ZnO phase. Thus it is clear that while PdZn is active for methanol steam reforming, the presence of ZnO seems necessary to maintaining catalyst stability. We have also explored role of ZnO particle size and morphology by mixing in a separate ZnO phase

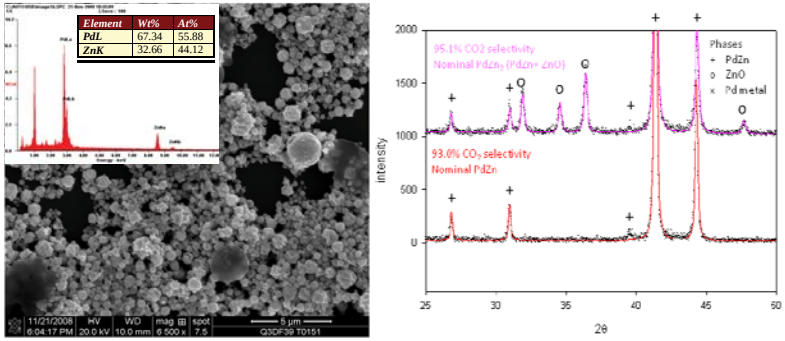

Figure 1 a) SEM and SED of 1:1 PdZn aerosol powder after reduction in 5% H_2 at 500°C for 4 hrs, b) XRD of 1:1 PdZn and 1:1.2 PdZn aerosol powder after reduction in 5% H_2 at 500°C for 4 hrs followed by on methanol reforming

Significance

It has long been known that bimetallic catalysts are necessary for many reactions. It is however difficult to determine the role of the oxide support since bimetallic catalysts are typically made by impregnating a metal onto an oxide. Here we show that a thermodynamically stable, unsupported alloy phase can be readily prepared via aerosol synthesis with adequate surface area for catalytic activity measurements. The synthesis method allows great flexibility in synthesizing a range of alloy compositions, and it is also possible to vary particle sizes by changing the aerosol generator and precursor concentrations. Our results demonstrate that both the metal alloy phases and supporting oxide are necessary for achieving a stable methanol steam reforming catalyst system.

References

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